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A CONSISTENT SET OF THERMODYNAMIC CONSTANTS FOR
AMERICIUM (III) SPECIES WITH HYDROXYL AND CARBONATE*

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Abstract

A consistent set of thermodynamic constants for aqueous species and compounds of Am(III) with hydroxyl and carbonate ligands has been developed. The procedure used to develop these constants involved establishing a value for one formation constant at a time in a sequential order, starting with the hydrolysis products and hydroxide solids, and then proceeding to carbonate species. The EQ3NR chemical-equilibrium model was used to test the constants developed. These constants are consistent with most of the experimental data that form their basis; however, considerable uncertainty still exists in some aspects of the Am(III) data.

Introduction

Americium is one of the major contributors to the radioactivity of high-level waste that will eventually be stored in geologic repositories. Under natural conditions, only one oxidation state of americium should exist, Am(III). To model the transport of americium in water, information is needed about aqueous species and solids of Am(III) that exist under repository conditions. Although numerous experimental studies have been done that contribute information about aqueous species and solids of americium, these data must be interpreted within a theoretical framework to assure that the data are internally consistent and to allow predictions under conditions that differ from the experiments. Thermodynamics provides the best framework for these data, as long as it is applicable, that is under equilibrium conditions.

This paper describes the development of a consistent set of thermodynamic constants for the formation of Am(III) complexes and solids with hydroxyl and carbonate ions. These anions are important because they form strong complexes with Am(III) and are present in most natural waters. Existing experimental data were used for this analysis. Because of disagreements among the results of some experiments, a set of thermodynamic constants that was consistent with all of the experimental data could not be developed.

Existing Experimental Data

Experimental data that form the basis for the constants developed here include distribution coefficients between organic and aqueous phases as a function of pH and carbonate content, potentiometric measurements as a function of pH, and solubility measurements as a function of pH and carbonate content.

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Experiments designed to determine hydrolysis constants are generally done in a neutral (noncomplexing) electrolyte to limit complex formation to hydrolysis products only. Two measurements of the distribution of Am(III) between organic and aqueous phases were used here. Lundqvist (1982) measured distribution coefficients in a perchlorate medium ($\mu = 1$ M) at pH 4 to 9 (μ is ionic strength and M is concentration in molar units). Caceci and Choppin (1983) measured distribution coefficients in a chloride medium ($\mu = 0.7$ M) at pH 5.9 and 8.1 as a function of oxalate content and determined the first hydrolysis constant from data for oxalate complexes using competing reactions. Another measurement of Am(III) distribution between organic and aqueous phases (Desire et al. 1969) was considered, but not included in the analysis. Data from two potentiometric titrations were also used. Nair et al. (1982) titrated Am(III) in perchlorate ($\mu = 1$ M) from pH 4 to 7. Edelstein et al. (1983) titrated two chemical analogs of Am(III) [Cm(III) and Nd(III)] in a chloride medium ($\mu = 0.1$ M). Hydrolysis constants and solubility-product constants can also be determined from solubility measurements. Four sets of solubility data for Am(III) in neutral electrolytes were considered. They include the measurements of Silva (1982) in perchlorate ($\mu = 0.1$ M) at pH 7 to 9.5; Rai et al. (1983) in chloride ($\mu = \sim 0.01$) at pH 7 to 13; Bernkopf and Kim (1984) in perchlorate ($\mu = 0.1$ to 0.3) at pH 6.5 to 13; and Nitsche and Edelstein (1985) in perchlorate ($\mu = 0.1$ M) at pH 7. Data for crystalline $\text{Am}(\text{OH})_3(\text{c})$ and amorphous $\text{Am}(\text{OH})_3(\text{am})$ hydroxide solids were reported. Significant differences among these results are apparent in a number of cases; choices made for this analysis are discussed in the following section.

Four sets of experimental data were used to determine constants for carbonate species with Am(III). Lundqvist (1982) measured Am(III) distribution between organic and aqueous phases in perchlorate ($\mu = 1$ M) at pH 4 to 7.5 under 0.1 and 1 atm CO_2 pressure. Bidoglio (1982) measured distribution coefficients in perchlorate ($\mu = 0.2$ M) at pH 8 to 9 and fixed total carbonate concentrations (1 to 6 mM); equilibrium CO_2 pressures were calculated to be 0.0001 to 0.001 atm. Silva and Nitsche (1983) measured the solubility of Am(III) in a carbonate solution under 0.008 atm CO_2 pressure at pH 6 ($\mu = 0.1$ M in perchlorate) and identified $\text{AmOHCO}_3(\text{c})$ as the solid. Bernkopf and Kim (1984) measured Am(III) solubility in carbonate solutions controlled by a CO_2 pressure of 0.00032 atm ($\mu = 0.1$ to 0.3 M in perchlorate) at pH 6 to 10.

Procedure

A variety of procedures can be used to determine one or more formation constants from a set of experimental data (Rossotti and Rossotti 1961). In the situation described here, where a large variety of data from different kinds of experiments was used, the procedure of employing a least-squares method or some equivalent technique to determine all the constants of a model in a single step did not seem practical. Instead, we tried to determine formation constants for one species at a time, in each case using only the experimental data that are sensitive to that species and previously determined formation constants. The EQ3NR chemical equilibrium model (Wolery 1983) was used to calculate experimentally observable parameters such as the distribution of Am(III) between organic and aqueous phases or the solubility of Am(III) under conditions applicable to the various experiments; these calculated values were compared with experimental data as a means of testing the formation constants.

The process started with the first hydrolysis constant of Am(III), which can be determined in a neutral electrolyte in a pH range where other hydrolysis products are not present in significant quantities. The formation constant for AmOH^{2+} was taken as the average of values reported by Lundqvist (1982), Caceci and Choppin (1983), Nair et al. (1982), and Edelstein et al. (1983), corrected to $\mu = 0$. The resulting logK is 7.41 (see Table I). EQ3NR calculations of the distribution experiments were done by defining fictitious species to simulate Am(III) in an organic phase and by estimating a logK for these species from the experimental distribution coefficients. Calculations of Am(III) distribution and average ligand number (for the potentiometric titrations) showed good agreement with the data of Lundqvist (1982) and Caceci and Choppin (1983), but underpredicted the average ligand number of Nair et al. (1982) over the pH range of 4 to 8.

Next, the availability of solubility data for $\text{Am(OH)}_3(\text{c})$ and $\text{Am(OH)}_3(\text{am})$ at pH 7 allowed solubility product constants for these solids to be determined in a pH range in which the first hydrolysis constant is the only important complex. Using the measured solubilities of Silva (1982) for $\text{Am(OH)}_3(\text{c})$ at pH 7, and of Rai et al. (1983) and Nitsche and Edelstein (1985) for $\text{Am(OH)}_3(\text{am})$ at pH 7, values of $\log K(\mu = 0)$ for the formation of these solids were calculated to be 26.60 and 25.10, respectively (see Table I).

Solubility data for $\text{Am(OH)}_3(\text{c})$ and $\text{Am(OH)}_3(\text{am})$ show that the solubility becomes constant for sufficiently high pH (see Fig. 1). This indicates that Am(OH)_3 is an important aqueous species but that Am(OH)_4^- is not present in significant amounts because formation of Am(OH)_4^- would increase solubility at high pH. Solubility data at high pH for either solid could be used to determine the formation constant of Am(OH)_3 , which is the only aqueous species present in significant quantity in the pH range where the solubility is constant; we used the solubility of $\text{Am(OH)}_3(\text{c})$ at pH 9.5 (Silva 1982) to determine logK for formation of Am(OH)_3 as 18.20 at $\mu = 0$ (see Table I).

TABLE I
FORMATION CONSTANTS OF Am(III) SPECIES AT ZERO IONIC STRENGTH

Reaction	logK
$\text{Am}^{3+} + \text{OH}^- \rightleftharpoons \text{AmOH}^{2+}$	7.41
$\text{Am}^{3+} + 2\text{OH}^- \rightleftharpoons \text{Am(OH)}_2^+$	<12.00
$\text{Am}^{3+} + 3\text{OH}^- \rightleftharpoons \text{Am(OH)}_3$	18.20
$\text{Am}^{3+} + 3\text{OH}^- \rightleftharpoons \text{Am(OH)}_3(\text{c})$	26.60
$\text{Am}^{3+} + 3\text{OH}^- \rightleftharpoons \text{Am(OH)}_3(\text{am})$	25.10
$\text{Am}^{3+} + \text{CO}_3^{2-} \rightleftharpoons \text{AmCO}_3$	8.26
$\text{Am}^{3+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{Am(CO}_3)_2$	13.30
$\text{Am}^{3+} + 3\text{CO}_3^{2-} \rightleftharpoons \text{Am(CO}_3)_3$	14.95
$\text{Am}^{3+} + \text{OH}^- + \text{CO}_3^{2-} \rightleftharpoons \text{AmOHCO}_3(\text{c})$	22.60

The formation constant for the second hydrolysis product, $\text{Am}(\text{OH})_2^+$, was determined by comparing the calculated solubilities with measurements taken by Rai et al. (1983) and Silva (1982) in the pH range of 8 to 9. This gave a value of $\log K$ for the formation of $\text{Am}(\text{OH})_2^+$ as ≤ 12.00 at $\mu = 0$ (see Table I).

Figure 1 shows the calculated solubility of $\text{Am}(\text{OH})_3(\text{c})$ and $\text{Am}(\text{OH})_3(\text{am})$ based on these constants (using EQ3NR) compared with experimental data. The data of Rai et al. (1983) are for amorphous material at low pH and crystalline at higher pH. Below pH 9.5, generally good agreement exists among the experiment comparisons, other than Bernkopf and Kim (1984), and between calculated and observed solubilities. Above pH 9.5, the calculated curve for crystalline material is about two orders of magnitude above that for the data from Rai et al. (1983). The data of Bernkopf and Kim (1984) are for amorphous material but have a lower solubility than either the crystalline or amorphous solids of other experiments. These data were not used in this analysis because they disagree with the generally consistent data of other experimenters and because the solid phase used in their work was not identified. Figure 2 shows a plot of the distribution of aqueous species in a neutral electrolyte calculated using the data in Table I.

After formation constants for Am(III) species in a neutral electrolyte were established, species with carbonate were considered next. The species AmCO_3^+ and $\text{Am}(\text{CO}_3)_2^-$ were considered first because they were identified by

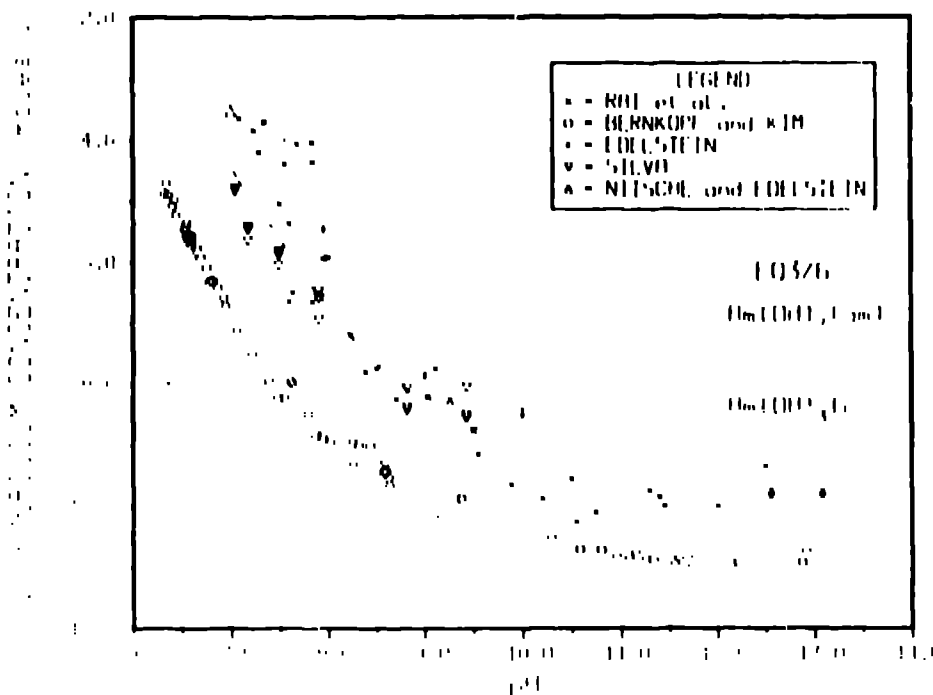


Fig. 1. Am(III) solubility in a neutral electrolyte at 25°C.

Lundqvist (1982) as being present under the conditions of his experiments; $\text{Am}(\text{CO}_3)_2^-$ was also identified by Bidoglio (1982) as the most important carbonate complex in his experiments. These species have also been identified for trivalent rare earths (Ferri et al. 1983; Lundqvist 1982). The value of $\log K$ for the formation of AmCO_3^+ was taken from Lundqvist (1982) and corrected to $\mu = 0$, giving a corrected value of 8.26; the value for $\text{Am}(\text{CO}_3)_2^-$ was taken as an average of the values reported by Lundqvist (1982) and Bidoglio (1982), corrected to $\mu = 0$, to give 13.30 (see Table I). Comparisons of experimental data with the calculated (with EQ3NR) distribution of Am(III) between organic and aqueous phases under the conditions of these two experiments gave generally good agreement using only these two carbonate species; it was not necessary to include the bicarbonate or hydroxy-carbonate complexes postulated by Bidoglio (1982) and by Bernkopf and Kim (1984).

These two Am(III)-carbonate complexes and the solubility data of Silva and Nitsche (1983) at pH 6 were used to calculate $\log K$ for $\text{AmOHCO}_3(\text{c})$ at $\mu = 0$, giving a value of 22.60 (see Table I). Because these measurements were made at only one pH, the one used to determine the formation constant, further comparisons between calculated and measured data could not be made. However, the solubility measurements of Bernkopf and Kim (1984) in carbonate solution also involved $\text{AmOHCO}_3(\text{c})$. EQ3NR calculations of the solubility of $\text{AmOHCO}_3(\text{c})$ under the conditions of the Bernkopf and Kim (1984) experiment compared well with measurements up to about pH 8; above that pH however, the calculated solubility dropped below the measured data. By analogy with rare-earth carbonates, the presence of $\text{Am}(\text{CO}_3)_3^{3-}$ was postulated (Ferri et al. 1983), and a value of $\log K$ of 14.95 for formation of this species at

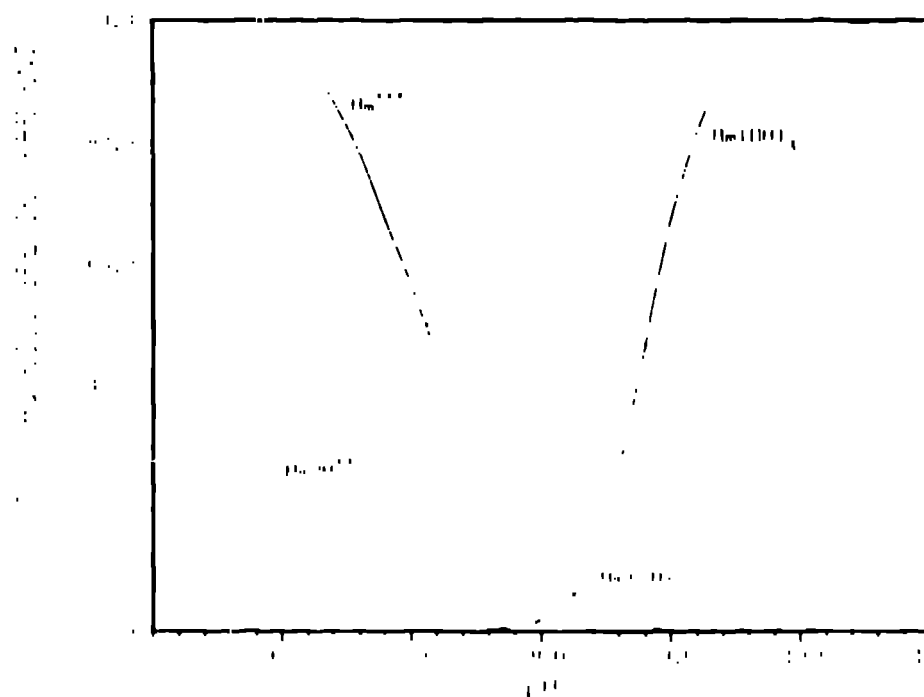


Fig. 2. Am(III) speciation in a neutral electrolyte at 25°C.

$\mu = 0$ was determined (see Table I). Use of this species along with the other two carbonate complexes gave generally good agreement between the calculated solubility and the measured data of Bernkopf and Kim (1984) (see Fig. 3). Figure 4 shows a distribution of species under the conditions of the Bernkopf and Kim (1984) solubility experiments; it differs significantly from that proposed by Bernkopf and Kim (1984). Only one hydrolysis product, AmOH^{2+} , is present in significant quantities; the importance of this species would be reduced at higher carbonate contents (higher equilibrium CO_2 pressures).

Problem Areas

Considerable uncertainty still exists in some aspects of Am(III) chemistry under natural conditions. One of the major areas of uncertainty is caused by disagreement among various experimenters about the identity of aqueous species present under the conditions of their experiments. Kerrisk (1984) pointed out that Lundqvist (1982) should have seen evidence of some of the Am(III) carbonate species reported by Bidoglio (1982); and likewise, Bidoglio (1982) should have seen some of the species reported by Lundqvist (1982). This situation occurs because the species used in these models have not been identified by some technique such as spectroscopy, but are inferred from the data. This situation will not be remedied until higher-sensitivity instruments, such as a photoacoustic spectrometer, are used to identify aqueous species.

A second problem area results from the disagreement among the various experiments about the solubility of Am(III) in a neutral electrolyte. Disagreements exist over the entire pH range (7 to 13) of the measurements (see Fig. 1). Part or all of these disagreements may have been caused by the different solid species controlling solubility in these experiments. Bernkopf and Kim (1984) did not report any identification of their solid: only a preparation technique. Silva (1982) identified his starting material as $\text{Am}(\text{OH})_3(\text{c})$ using x-ray data, but only visually compared the final solid to the starting material. Rai et al. (1983) saw evidence of an amorphous solid (probably $\text{Am}(\text{OH})_3(\text{am})$) at low pH and $\text{Am}(\text{OH})_3(\text{c})$ at high pH in the final material. Plots of the solubility data as a function of pH, taken from the experiments of Bernkopf and Kim (1984) and of Rai et al. (1983), show a break around pH 8.5 to 9.5, with a drop to lower solubilities at higher pH; this may be a signal of a change in the identity of the solid controlling solubility. This problem requires additional experimental work, giving strong emphasis to the identification of the solid phase or phases that control solubility under these conditions.

A final problem affecting the results reported here is the ionic-strength corrections to measured $\log K$ values. Many of the experiments discussed here were done at $\mu = 1 \text{ M}$; others ranged from $\mu = 0.7$ down to $\mu < 0.1$. Thermodynamic models such as EQ3NR use $\log K$ values at $\mu = 0$ and provide their own ionic-strength corrections. Experimentally derived activity coefficients were used to correct the measured values of $\log K$ to $\mu = 0$ (Robinson and Stokes 1959; Pitzer and Peiper 1980; Khoo et al. 1981; and Peiper and Pitzer 1982). Because of the high charge on Am^{3+} , activity coefficients of about 0.02 apply for this species at $\mu = 1 \text{ M}$. In comparing these activity coefficients with the values calculated by EQ3NR, the EQ3NR activity coefficients were found to be significantly different in a number of cases. For the EQ3NR

calculations discussed here, values of the β parameter used in the activity-coefficient calculation (Wolery 1983) were modified so that the calculated activity coefficients were comparable to experimentally derived values. This involved changing β as follows: from 8.0 Å to 5.0 Å for Am^{3+} , from 9.0 Å to 5.0 Å for H^+ , from 4.5 Å to 3.5 Å for CO_3^{2-} , from 4.5 Å to 4.0 Å for HCO_3^- , and from 3.0 Å to 4.0 Å for Cl^- . This type of correction, which is needed to adjust data measured over a range of ionic strengths to some common value, adds additional uncertainty to the results.

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